

PHOTOSENSITIVE COMPOSITION FOR INTERLAYER DIELECTRIC  
AND METHOD OF FORMING PATTERNED INTERLAYER  
DIELECTRIC

5      Technical Field

The present invention relates to an improvement in a photosensitive composition, particularly a photodecomposable polysilsesquiazane composition that can yield a film which can be finely patterned with high resolution upon exposure to light,  
10 and a method for forming a patterned interlayer insulation film using this composition.

Background Art

In the manufacture of semiconductor devices and liquid  
15 crystal display devices, an interlayer insulation film is used. In general, an interlayer insulation film is formed by coating or deposition from a gaseous phase, and is then etched through a photoresist to form a pattern. In the case of a fine pattern, however, gaseous phase etching is used. This etching, however,  
20 suffers from problems of high apparatus cost and slow processing speed.

On the other hand, the interlayer insulation film is exposed to a high temperature above 400°C during the device manufacture process. Therefore, organic resins as used in  
25 conventional resists cannot withstand the high temperature and thus cannot be used as the interlayer insulation film. Patterned silica-based ceramic films are known to be useful as a film, capable of meeting the above material requirement, excellent in heat resistance as well as in abrasion resistance, corrosion  
30 resistance, insulating properties, transparency and the like for semiconductor devices, liquid crystal display devices, printed circuit boards and the like.

In particular, when a patterned film is allowed to remain unremoved for use as an interlayer insulation film, the film  
35 preferably has low permittivity. In order to meet the above requirement, Japanese Patent Laid-Open No. 181069/2000

discloses a method for forming a patterned polysilazane film, comprising the steps of: forming a coating of a photosensitive polysilazane composition comprising polysilazane and a photoacid generating agent; exposing the coating pattern-wise to light; and dissolving and removing the coating in its exposed area. This publication also discloses a method for forming a patterned insulating film, comprising the step of subjecting the above patterned polysilazane film to standing in an ambient atmosphere or baking to convert the polysilazane film to a silica-based ceramic film.

Further, the applicant of this invention has found that a composition prepared by adding a water-soluble compound as a shape stabilizer to a photosensitive composition comprising a specific modified polysilsesquiazane and a photoacid generating agent can enhance the resolution and, in addition, can form a fine pattern of an interlayer insulation film possessing excellent permittivity and mechanical properties. The applicant has proposed the above finding as Japanese Patent Application No. 297107/2000. Specifically, the applicant has proposed a photosensitive composition for an interlayer insulation film, comprising: a modified polysilsesquiazane comprising basic constitutional units having a number average molecular weight of 100 to 100,000 and represented by formula  $-\text{[SiR}^1(\text{NR}^2)_{1.5}\text{]}-$  and 0.1 to 100% by mole, based on the above basic constitutional units, of other constitutional units represented by formulae  $-\text{[SiR}^1_2\text{NR}^2\text{]}-$  and/or  $-\text{[SiR}^1_3(\text{NR}^2)_{0.5}\text{]}-$  wherein R<sup>1</sup>'s each independently represent an alkyl group having 1 to 3 carbon atoms or a substituted or unsubstituted phenyl group and R<sup>2</sup>'s each independently represent hydrogen, an alkyl group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group; a photoacid generating agent; and a water-soluble compound as a shape stabilizer. The applicant has further proposed a method for forming a patterned interlayer insulation film, characterized by comprising the steps of: forming a coating of the above photosensitive composition for an interlayer insulation film; exposing the coating pattern-wise to

light; dissolving and removing the coating in its exposed area; and subjecting the residual patterned coating to standing in an ambient atmosphere or baking.

The use of the above-described photosensitive composition can eliminate the need to conduct gaseous phase etching and can form an interlayer insulation film having a fine pattern at a low cost. On the other hand, the photosensitive composition described in Japanese Patent Laid-Open No. 181069/2000 has a problem of storage stability. Further, when the above photosensitive compositions are used to form a thick interlayer insulation film, cracking is likely to occur. Therefore, an improvement in film thickness limit is desired. Further, in this case, it is also required that the film thickness limit be improved without sacrificing the photosensitivity of the photosensitive composition and the hardness of the formed interlayer insulation film. An additional problem is that, upon patterning of these interlayer insulation films, at exposed areas, an acid produced from the photoacid generating agent is diffused in nonexposed areas where the acid cleaves Si-N bond of the modified polysilsesquiazane, disadvantageously resulting in a change in dimension of the pattern with the elapse of time.

#### Disclosure of the Invention

The present inventor has made extensive and intensive studies with a view to solving the above problems of the prior art and, as a result, has found that the replacement of a part of constitutional units of polysilsesquiazane by a linking group other than the silazane bond can enhance the storage stability of a photosensitive composition without sacrificing the photosensitivity of the photosensitive composition and the hardness of an interlayer insulation film formed from the photosensitive composition, that the selection of the alternative linking group can enhance the film thickness limit of the interlayer insulation film formed from the photosensitive composition, and, further, that the addition of a basic material can also prevent a change in dimension of a pattern caused by

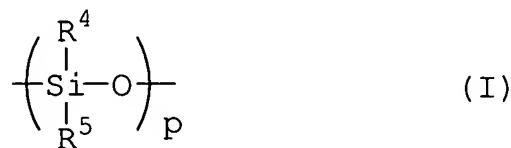
diffusion of the acid produced in the exposed areas. This has led to the completion of the present invention.

The constitution of the present invention will be described.

5 [1] A photosensitive composition for an interlayer insulation film, characterized by comprising: a modified polysilsesquiazane having a weight average molecular weight of 500 to 200,000 comprising basic constitutional units represented by formula  $-[\text{SiR}^1(\text{NR}^2)_{1.5}]-$  wherein R<sup>1</sup>'s each 10 independently represent an alkyl group having 1 to 3 carbon atoms or a substituted or unsubstituted phenyl group; R<sup>2</sup>'s each independently represent hydrogen, an alkyl group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group, up to 50% by mole of said basic constitutional units having 15 been replaced by a linking group other than the silazane bond; a photoacid generating agent; and a basic material.

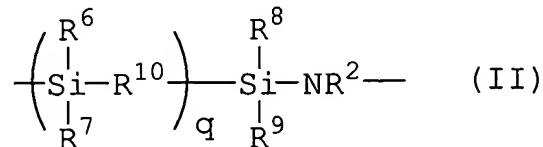
[2] The photosensitive composition for an interlayer insulation film according to the above item [1], wherein said modified polysilsesquiazane further comprises 0.1 to 100% by 20 mole, based on said basic constitutional units, of other constitutional units represented by formulae  $-[\text{SiR}^3_2\text{NR}^2]-$  and/or  $[\text{SiR}^3_3(\text{NR}^2)_{0.5}]-$  wherein R<sup>3</sup>'s each independently represent hydrogen, an alkyl group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group; and R<sup>2</sup>'s each 25 independently represent hydrogen, an alkyl group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group.

[3] The photosensitive composition for an interlayer insulation film according to the above item [1] or [2], wherein said linking group is represented by formula (I):



wherein R<sup>4</sup> and R<sup>5</sup> each independently represent hydrogen, or an alkyl, alkenyl, cycloalkyl, aryl, aralkyl, alkylamino, alkylsilyl, or alkoxy group; and p is an integer of 1 to 10.

[4] The photosensitive composition for an interlayer insulation film according to the above item [1] or [2], wherein said linking group is represented by formula (II):



5       wherein R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup> each independently represent an alkyl, alkenyl, cycloalkyl, aryl, aralkyl, alkylamino, alkylsilyl, or alkoxy group; R<sup>10</sup> represents an oxygen atom or an alkylene, alkenylene, cycloalkylene, arylene, alkylimino, or alkylsilylene group; R<sup>2</sup>'s each independently represent hydrogen, an alkyl 10 group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group; and q is an integer of 1 to 10.

10      [5] The photosensitive composition for an interlayer insulation film according to the above item [4], wherein R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup> represent a methyl group, R<sup>10</sup> represents a phenylene group, R<sup>2</sup> represents hydrogen, and q is 1.

15      [6] The photosensitive composition for an interlayer insulation film according to any one of the above items [1] to [5], wherein said photoacid generating agent is selected from the group consisting of sulfoxime compounds and triazine 20 compounds.

20      [7] The photosensitive composition for an interlayer insulation film according to any one of the above items [1] to [6], wherein said basic material is selected from the group consisting of higher amines, hindered amines, and 25 alkanolamines.

25      [8] The photosensitive composition for an interlayer insulation film according to any one of the above items [1] to [7], which further comprises 0.1 to 40% by mass, based on the photosensitive composition, of a dissolution preventive selected 30 from the group consisting of t-butoxycarbonylated catechol, t-butoxycarbonylated hydroquinone, t-butyl benzophenone-4,4'-dicarboxylate, and t-butyl 4,4'-oxydibenzene.

35      [9] The photosensitive composition for an interlayer

insulation film according to any one of the above items [1] to [8], which further comprises a nitro- or carbonic ester-containing water-soluble compound as a shape stabilizer.

[10] The photosensitive composition for an interlayer insulation film according to any one of the above items [1] to [9], which further comprises a sensitizing dye.

[11] A method for forming a patterned interlayer insulation film, characterized by comprising: forming a coating of a photosensitive composition for an interlayer insulation film, comprising a modified polysilsesquiazane, a photoacid generating agent, and a basic material, said modified polysilsesquiazane having a weight average molecular weight of 500 to 200,000 comprising basic constitutional units represented by formula  $-\text{[SiR}^1(\text{NR}^2)_{1.5}\text{]}-$  wherein R<sup>1</sup>'s each independently represent an alkyl group having 1 to 3 carbon atoms or a substituted or unsubstituted phenyl group, R<sup>2</sup>'s each independently represent hydrogen, an alkyl group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group, up to 50% by mole of said basic constitutional units having been replaced by a linking group other than a silazane bond; exposing said coating pattern-wise to light; dissolving and removing the coating in its exposed area; and subjecting the residual patterned coating in an ambient atmosphere to standing or baking.

The present invention will be described in more detail.

#### Best Mode for Carrying Out the Invention

The photosensitive composition for an interlayer insulation film according to the present invention is a polysilsesquiazane-type positive-working photoresist. Upon exposure of a coating of the photosensitive composition to light in a pattern-wise manner, Si-N bonds of the polysilsesquiazane in the exposure area of the coating are cleaved, and the cleaved parts are further reacted with moisture in an ambient atmosphere to give silanol (Si-OH) bonds. That is, when the coating after the exposure is developed, the photosensitive

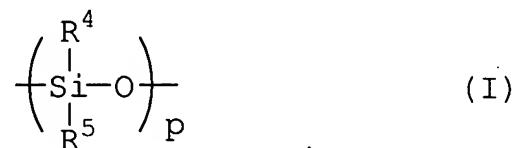
composition in its exposed area is dissolved and removed while the unexposed area stays on the substrate to form a pattern (a positive-working pattern). Thus, the photosensitivity of the polysilsesquiazane-type positive-working photoresist is relied upon the Si-N bonds as basic constitutional units of the polysilsesquiazane-type positive-working photoresist. Therefore, the replacement of a part of the Si-N bonds by a linking group other than the silazane bond reduces the number of Si-N bonds which are sites cleaved upon exposure. This is considered to result in lowered photosensitivity of the polymer per se. However, it has been found that, even when all the Si-N bonds are not converted to Si-OH bonds, in the subsequent development treatment, the exposed area is completely removed as a mass comprised of a plurality of basic constitutional units. That is, it has been found that, even when a part of the basic constitutional units of polysilsesquiazane is replaced by a nonphotosensitive bond other than the Si-N bond, the photosensitivity as the photoresist can be satisfactorily ensured without sacrificing the removability of the exposed area.

Based on such finding, according to the present invention, the modification of polysilsesquiazane on a level, which does not sacrifice the photosensitivity of the photosensitive composition as a photoresist, can enhance the storage stability of the photosensitive composition and, at the same time, can realize an improvement in film thickness limit of an interlayer insulation film formed upon conversion of the photosensitive composition film to a ceramic while maintaining high hardness.

The modified polysilsesquiazane contained in the photosensitive composition for an interlayer insulation film according to the present invention comprises basic constitutional units represented by formula  $-[SiR^1(NR^2)_{1.5}]-$ . Up to 50% by mole of the basic constitutional units have been replaced by a linking group other than the silazane bond. In the formula, R<sup>1</sup>'s each independently represent an alkyl group having 1 to 3 carbon atoms or a substituted or unsubstituted phenyl group; and R<sup>2</sup>'s each independently represent hydrogen,

an alkyl group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group. Preferably, R<sup>1</sup> represents a methyl or phenyl group, most preferably a methyl group. Preferably, R<sup>2</sup> represents hydrogen.

5       The linking group, by which up to 50% by mole of the basic constitutional units is replaced, may be one represented by formula (I):

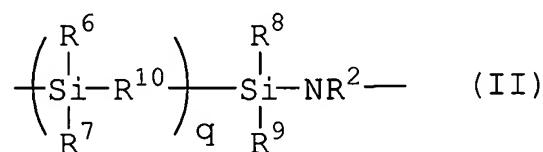


wherein R<sup>4</sup> and R<sup>5</sup> each independently represent hydrogen, or  
 10      an alkyl, alkenyl, cycloalkyl, aryl, aralkyl, alkylamino, alkylsilyl,  
         or alkoxy group; and p is an integer of 1 to 10. The  
     replacement of the above basic constitutional units by this  
     linking group can improve the storage stability of the  
     photosensitive composition. The reason for this is believed to  
 15      be as follows. In the case of polysilsesquiazane consisting of  
     basic constitutional units in a trifunctional form alone, a number  
     of distorted cyclic structures, which are cleaved during storage,  
     are present in its molecule and cleaved parts recombine with  
     similarly cleaved other molecules to increase the molecular  
 20      weight. On the other hand, the replacement of a part of the  
     basic constitutional units by a linking group other than the  
     silazane bond can reduce the number of distorted cyclic  
     structures. This is considered to suppress an increase in  
     molecular weight caused by the above cleavage and  
 25      recombination.

R<sup>4</sup> and R<sup>5</sup> generally represent an alkyl group having 1 to 7 carbon atoms, preferably 1 to 5 carbon atoms, more preferably 1 or 2 carbon atoms, an alkenyl group having 2 to 7 carbon atoms, a cycloalkyl group having 5 to 7 carbon atoms, or an aryl group. More specific examples of R<sup>4</sup> and R<sup>5</sup> include phenyl, tolyl, xylyl, cumenyl, benzyl, phenethyl, α-methylbenzyl, benzhydryl, trityl, styryl, cinnamyl, biphenyl, and naphthyl groups. The alkylsilyl group (mono-, di-, or tri-substituted),

the alkylamino group (mono- or di-substituted), and the alkoxy group generally have 1 to 7 carbon atoms. R<sup>4</sup> and R<sup>5</sup> may be the same or different. p is preferably 1 to 5, most preferably 2.

According to the present invention, as described above, 5 an enhancement in storage stability of the photosensitive composition and, at the same time, an enhancement in film thickness limit of an interlayer insulation film formed from the photosensitive composition without sacrificing the hardness of the interlayer insulation film can be realized by using, as the 10 above linking group, a group represented by formula (II):



wherein R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup> each independently represent an alkyl, alkenyl, cycloalkyl, aryl, aralkyl, alkylamino, alkylsilyl, or alkoxy group; R<sup>10</sup> represents an oxygen atom or an alkylene, 15 alkenylene, cycloalkylene, arylene, alkylimino, or alkylsilylene group; R<sup>2</sup>'s each independently represent hydrogen, an alkyl group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group; and q is an integer of 1 to 10.

R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup> generally represent an alkyl group 20 having 1 to 7 carbon atoms, preferably 1 to 5 carbon atoms, more preferably 1 or 2 carbon atoms (particularly a methyl group), an alkenyl group having 2 to 7 carbon atoms, a cycloalkyl group having 5 to 7 carbon atoms, or an aryl group. More specific examples of R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup> include phenyl, 25 tolyl, xylyl, cumenyl, benzyl, phenethyl, α-methylbenzyl, benzhydryl, trityl, styryl, cinnamyl, biphenyl, and naphthyl groups. The alkylsilyl group (mono-, di-, or tri-substituted), the alkylamino group (mono- or di-substituted), and the alkoxy group generally have 1 to 7 carbon atoms. R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup> 30 may be the same or different. R<sup>10</sup> generally represents an alkylene group having 1 to 7 carbon atoms, preferably 1 to 5 carbon atoms, more preferably 1 or 2 carbon atoms, an alkenylene group having 2 to 7 carbon atoms, a cycloalkylene

group having 5 to 7 carbon atoms, an arylene group, an alkylimino group having 1 to 7 carbon atoms, or an alkylsilylene group having 1 to 7 carbon atoms. More specific examples thereof include phenylene, tolylene, xylylene, benzylidene,  
5 phenethylidene,  $\alpha$ -methylbenzylidene, cinnamylidene, and naphthylene groups. The arylene group is particularly preferably a phenylene group. Preferably, R<sup>2</sup> represents hydrogen. q is preferably 1 to 5, most preferably 1.

Up to 50% by mole of the basic constitutional units of the  
10 polysilsesquiazane has been replaced by the linking group other than the silazane bond. Effects of the present invention, that is, an improvement in storage stability of the photosensitive composition according to the present invention and, for some linking groups, an improvement in film thickness limit, can be  
15 attained by the presence of the linking group. Therefore, there is no need to specify the lower limit of the percentage replacement as a technical idea. In order to attain the effects of the present invention on a satisfactory level, however, in general, the percentage replacement of the basic constitutional  
20 units by the linking group is suitably not less than 0.1% by mole, preferably not less than 1% by mole. On the other hand, in general, the upper limit of the percentage replacement is suitably not more than 50% by mole, preferably not more than 45% by mole, more preferably not more than 40% by mole,  
25 from the viewpoint of avoiding the sacrifice of desired photosensitivity of the photosensitive composition for an interlayer insulation film. The form of replacement of the basic constitutional units by the linking group according to the present invention is random. Further, in the modified  
30 polysilsesquiazane according to the present invention, the linking group represented by formula (I) and the linking group represented by formula (II) may be present in a mixed form.

The modified polysilsesquiazane according to the present invention may further comprise 0.1 to 100% by mole, based on  
35 the basic constitutional units, of other constitutional units represented by formulae  $-\text{[SiR}^3_2\text{NR}^2\text{]}-$  and/or  $[\text{SiR}^3_3(\text{NR}^2)_{0.5}\text{]}-$

wherein R<sup>3</sup>'s each independently represent hydrogen, an alkyl group having 1 to 3 carbon atoms, or a substituted or unsubstituted phenyl group; and R<sup>2</sup>'s each independently represent hydrogen, an alkyl group having 1 to 3 carbon atoms,  
5 or a substituted or unsubstituted phenyl group. As compared with the polysilsesquiazane comprised of trifunctional basic constitutional units alone, the replacement of the basic constitutional units by the difunctional constitutional units and/or the monofunctional constitutional units can suppress an  
10 increase in molecular weight of the polysilsesquiazane and can further enhance the storage stability of the photosensitive composition.

These other constitutional units are randomly bonded to the basic constitutional units. Each of R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> may be  
15 independently selected. Therefore, each of these groups may be the same or different between basic constitutional units. Further, each of them may be the same or different between basic constitutional units and other constitutional units. For example, possible embodiments include one wherein, in the  
20 basic constitutional units, a part of R<sup>1</sup> represents methyl with the remaining R<sup>1</sup> representing phenyl, one wherein, in the basic constitutional units, a part of R<sup>2</sup> represents hydrogen with the remaining R<sup>2</sup> representing methyl, one wherein R<sup>1</sup> in the basic constitutional units represents methyl while R<sup>3</sup> in other  
25 constitutional units represents methyl or phenyl, one wherein R<sup>2</sup> in the basic constitutional units represents hydrogen while R<sup>3</sup> in other constitutional units represents hydrogen or methyl. Preferably, for both the basic constitutional units and the other constitutional units, R<sup>1</sup> and R<sup>3</sup> represent a methyl or phenyl  
30 group, most preferably a methyl group. Further, for both the basic constitutional units and the other constitutional units, preferably, R<sup>2</sup> represents hydrogen.

The modified polysilsesquiazane comprising the above other constitutional units comprises 0.1 to 100% by mole, preferably 0.5 to 40% by mole, more preferably 1 to 20% by mole, based on the basic constitutional units, of other

constitutional units represented by formulae  $-[\text{SiR}^3_2\text{NR}^2]-$  and/or  $[\text{SiR}^3_3(\text{NR}^2)_{0.5}]-$ . When only constitutional units represented by formula  $-[\text{SiR}^3_2\text{NR}^2]-$  are contained as other constitutional units, the content of the constitutional units based on the basic constitutional units is preferably 0.1 to 100% by mole, more preferably 1 to 20% by mole. On the other hand, when only constitutional units represented by formula  $[\text{SiR}^3_3(\text{NR}^2)_{0.5}]-$  are contained as other constitutional units, the content of the constitutional units based on the basic constitutional units is preferably 0.1 to 50% by mole, more preferably 0.5 to 20% by mole. When the content of these other constitutional units exceeds 100% by mole, the molecular weight of the polymer is not satisfactorily high. Consequently, disadvantageously, the coating becomes fluid.

The weight average molecular weight of the modified polysilsesquiazane according to the present invention is in the range of 500 to 200,000, preferably 600 to 150,000. When the weight average molecular weight of the modified polysilsesquiazane is smaller than 500, the coating becomes fluid. On the other hand, when the weight average molecular weight of the modified polysilsesquiazane is larger than 200,000, the dissolution of the photosensitive composition in a solvent is difficult. Both the above cases are unfavorable.

The modified polysilsesquiazane according to the present invention can be easily prepared by, in ammonolysis for synthesizing conventional polysilazane, using, as starting materials,  $\text{R}^1\text{SiCl}_3$  and a monomer, from which a linking group other than a silazane bond may be derived, so that the molar ratio of the monomer used corresponds to the replacement ratio of the linking group. For example, when the linking group to be incorporated is a group represented by formula (I), ammonolysis may be carried out using a silane starting material prepared by mixing  $\text{Cl}(\text{Si}(\text{R}^4)(\text{R}^5)\text{O})_p\text{Si}(\text{R}^1)\text{Cl}_2$  into  $\text{R}^1\text{SiCl}_3$ . In this case, in calculating the molar ratio corresponding to the replacement ratio of the linking group, the numeric value  $p$  in the monomer should be taken into consideration because the

Si(R<sup>1</sup>)Cl<sub>2</sub> part of Cl(Si(R<sup>4</sup>)(R<sup>5</sup>)O)<sub>p</sub>Si(R<sup>1</sup>)Cl<sub>2</sub> is incorporated in the basic constitutional units. For example, in the case of p = 1, when R<sup>1</sup>SiCl<sub>3</sub> and ClSi(R<sup>4</sup>)(R<sup>5</sup>)OSi(R<sup>1</sup>)Cl<sub>2</sub> are mixed together in a molar ratio of 1 : 1, the replacement ratio of the linking group  
5 is about 33%. In the case of p = 2, when R<sup>1</sup>SiCl<sub>3</sub> and Cl(Si(R<sup>4</sup>)(R<sup>5</sup>)O)<sub>2</sub>Si(R<sup>1</sup>)Cl<sub>2</sub> are mixed together in a molar ratio of 2 : 1, the replacement ratio of the linking group is 40%. On the other hand, when the linking group represented by formula  
10 (II) is contained as the linking group, ammonolysis may be carried out using a starting material prepared by mixing R<sup>1</sup>SiCl<sub>3</sub> and Cl(Si(R<sup>6</sup>)(R<sup>7</sup>)R<sup>10</sup>)<sub>q</sub>Si(R<sup>8</sup>)(R<sup>9</sup>)Cl in a molar ratio corresponding to the replacement ratio of the linking group independently of the q value. For example, when the former and the latter are mixed together in a molar ratio of 9 : 1, the  
15 replacement ratio of the linking group is 10%.

The modified polysilsesquiazane containing the above other constitutional units can be easily prepared by, in ammonolysis for synthesizing conventional polysilazane, using R<sup>1</sup>SiCl<sub>3</sub>, R<sup>1</sup><sub>2</sub>SiCl<sub>2</sub> and/or R<sup>1</sup><sub>3</sub>SiCl as starting materials so that  
20 R<sup>1</sup><sub>2</sub>SiCl<sub>2</sub> and R<sup>1</sup><sub>3</sub>SiCl are used in a molar ratio corresponding to the content ratio of the above other constitutional units. For example, when 20% by mole of constitutional units represented by formula -[SiR<sup>1</sup><sub>2</sub>NR<sup>2</sup>]- is contained as other constitutional units, ammonolysis may be carried out using a silane starting  
25 material prepared by mixing 20% by mole of R<sup>1</sup><sub>2</sub>SiCl<sub>2</sub> into R<sup>1</sup>SiCl<sub>3</sub>. Likewise, when 10% by mole of constitutional units represented by formula [SiR<sup>1</sup><sub>3</sub>(NR<sup>2</sup>)<sub>0.5</sub>]- is contained as other constitutional units, 10% by mole of R<sup>1</sup><sub>3</sub>SiCl may be mixed into R<sup>1</sup>SiCl<sub>3</sub>.

30 For details of ammonolysis in synthesizing polysilazane, reference may be made, for example, to Japanese Patent Publication No. 16325/1988.

The photosensitive composition according to the present invention contains a photoacid generating agent. The  
35 photoacid generating agent is brought into an excited state directly by exposure to light in its inherent photosensitive

wavelength region. Alternatively, when a sensitizing dye is used, the photoacid generating agent is brought into an excited state indirectly by exposure to light in its wavelength region which can excite the sensitizing dye. The excited photoacid 5 generating agent cleaves Si-N bonds in the modified polysilsesquiazane, and the cleaved parts are considered to be reacted with moisture in the atmosphere to give silanol (Si-OH) bonds. Since the silanol is soluble in a developer which will be described later, the coating of the photosensitive composition 10 only in its light exposed area is dissolved and removed to provide positive-working patterning.

The photoacid generating agent may be a peroxide. Specific examples of peroxides as the photoacid generating agent include 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone, t-butylperoxybenzoate, methyl ethyl ketone peroxide, cyclohexanone peroxide, methylcyclohexanone peroxide, methyl acetoacetate peroxide, acetylacetone peroxide, 1,1-bis(t-hexylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-hexylperoxy)cyclohexane, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, di-t-butylperoxy-2-methylcyclohexane, 1,1-bis(t-butylperoxy)cyclododecane, 2,2-bis(t-butylperoxy)butane, n-butyl 4,4-bis(t-butylperoxy)valerate, 2,2-bis(4,4-di-t-butylperoxy)cyclohexyl)propane, p-menthanehydroperoxide, diisopropylbenzenehydroperoxide, 1,1,3,3-tetramethylbutylhydroperoxide, cumene hydroperoxide, t-hexylhydroperoxide, t-butylhydroperoxide,  $\alpha,\alpha'$ -bis(t-butylperoxy)diisopropylbenzene, dicumyl peroxide, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane, t-butylcumyl peroxide, di-t-butyl peroxide, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexyne-3, isobutylyl peroxide, 3,5,5-trimethylhexanoyl peroxide, octanoyl peroxide, lauroyl peroxide, stearoyl peroxide, succinic acid peroxide, m-toluoylbenzoyl peroxide, benzoyl peroxide, di-n-propylperoxydicarbonate, diisopropylperoxydicarbonate, bis(4-t-butylcyclohexyl)peroxydicarbonate, di-2-

ethoxyethylperoxydicarbonate, di-2-  
 ethylhexylperoxydicarbonate, di-3-  
 methoxybutylperoxydicarbonate, di(3-methyl-3-  
 methoxybutyl)peroxydicarbonate,  $\alpha,\alpha'$ -  
 5 bis(neodecanoylperoxy)diisopropylbenzene,  
 cumylperoxyneodecanoate, 1,1,3,3-  
 tetramethylbutylperoxyneodecanoate, 1-cyclohexyl-1-  
 methylethylperoxyneodecanoate, t-hexylperoxyneodecanoate, t-  
 butylperoxyneodecanoate, t-hexylperoxypivalate, t-  
 10 butylperoxypivalate, 1,1,3,3-tetramethylbutylperoxy-2-  
 ethylhexanoate, 2,5-dimethyl-2,5-bis(2-  
 ethylhexanoylperoxy)hexane, 1-cyclohexyl-1-  
 methylethylperoxy-2-ethylhexanoate, t-hexylperoxy 2-  
 ethylhexanoate, t-butylperoxy 2-ethylhexanoate, t-  
 15 butylperoxyisobutyrate, t-hexylperoxyisopropylmonocarbonate,  
 t-butylperoxymaleic acid, t-butylperoxy 3,5,5-  
 trimethylhexanoate, t-butylperoxylaurate, 2,5-dimethyl-2,5-(m-  
 toluoylperoxy)hexane, t-butylperoxyisopropylmonocarbonate, t-  
 butylperoxy 2-ethylhexylmonocarbonate, t-hexylperoxybenzoate,  
 20 2,5-dimethyl-2,5-bis(benzoylperoxy)hexane, t-  
 butylperoxyacetate, t-butylperoxy-m-toluoylbenzoate, bis(t-  
 butylperoxy)isophthalate, t-butylperoxyallylmonocarbonate, t-  
 butyltrimethylsilyl peroxide, and 1,3-di(t-  
 butylperoxycarbonyl)benzene.

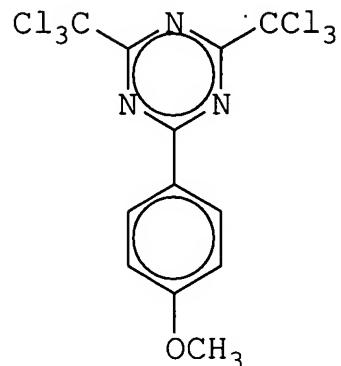
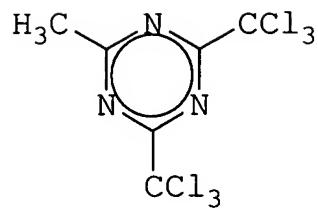
25 The photoacid generating agent may be a naphthoquinonediazidosulfonic ester or a nitrobenzyl ester. Specific examples of naphthoquinonediazidosulfonic esters as the photoacid generating agent include 1,2-naphthoquinone-(2)-diazido-5-sulfonic acid chloride, 1,2-naphtoquinone-(2)-diazido-4-sulfonic acid chloride, an (mono- to tri-) ester of 2,3,4-trihydroxybenzophenon with 6-diazo-5,6-dihydro-5-oxo-naphthalene-1-sulfonic acid, and an (mono- to tri-) ester of 2,3,4,4'-trihydroxybenzophenon with 6-diazo-5,6-dihydro-5-oxo-naphthalene-1-sulfonic acid. Specific examples of nitrobenzyl esters as the photoacid generating agent include nitrobenzyl tosylate, dinitrobenzyl tosylate, nitrobenzyl chloride,

dinitrobenzyl chloride, nitrobenzyl bromide, dinitrobenzyl bromide, nitrobenzyl acetate, dinitrobenzyl acetate, nitrobenzyltrichloroacetate, and nitrobenzyltrifluoroacetate. Other useful photoacid generating agents include benzoin 5 tosylate, nitrobenzylsulfonic acids, and onium salts (for example, bis(4-t-butylphenyl)iodonium salt and triphenyl sulfonium salt). If necessary, these photoacid generating agents may be used in combination.

In the photosensitive composition according to the 10 present invention, the photoacid generating agent is generally contained in an amount of 0.05 to 50% by mass based on the mass of the modified polysilsesquiazane, depending upon the type and applications. When the content of the photoacid generating agent is less than 0.05% by mass, the 15 decomposition reaction rate is very low. On the other hand, when the content of the photoacid generating agent is more than 50% by mass, a dense film which is a modified polysilsesquiazane-derived feature cannot be formed without difficulties. The content of the photoacid generating agent is 20 preferably 0.1 to 20% by mass, more preferably 1 to 20% by mass, based on the mass of the modified polysilsesquiazane.

When the photosensitive composition comprising the modified polysilsesquiazane and the photoacid generating agent should be stored for a given period of time or longer, some 25 photoacid generating agents including nitrobenzylsulfonic esters have a fear of being decomposed by a very small amount of NH<sub>3</sub> liberated from the modified polysilsesquiazane during storage. In this case, the selection of a base-resistant photoacid generating agent can improve the storage stability of the 30 photosensitive composition. Base-resistant photoacid generating agents include iminosulfonate derivatives, disulfone derivatives, diazomethane derivatives, and other photoacid generating agents, for example, sulfoxime compounds such as 4-methoxy- $\alpha$ -(((4- 35 methoxyphenyl)sulfonyl)oxy)imino)benzeneacetonitrile and triazine compounds such as compounds represented by the

following formula.



The photosensitive composition according to the present invention contains a basic material. When the basic material is contained, a change in dimension of the pattern caused by diffusion of an acid, produced from the photoacid generating agent in exposed areas in patterning of a thin film of the photosensitive composition, into nonexposed areas can be prevented.

The basic material may be any material so far as it can neutralize the acid produced from the photoacid generating agent. However, the use of amines having a certain high level of boiling point such as higher amines, hindered amines, and alkanolamines is preferred from the viewpoint of avoiding such an unfavorable phenomenon that the basic material is easily evaporated from a coating at the time of coating of the photosensitive composition and prebaking the coating.

Preferably, higher amines have a boiling point of 50°C or above, more preferably 70°C or above. The higher amine may be any of primary, secondary, and tertiary amines. Among them, secondary amines are suitable. The higher amine having the above boiling point generally contains 4 or more, preferably 6 or more carbon atoms. Specific examples of higher amines

include didodecylamine, didecylamine, dioctylamine, n-butylamine, sec-butylamine, dibutylamine, and tributylamine.

Various hindered amines may be used independently of whether they are monomers or polymers. Specific examples of hindered amines include: poly[(6-morpholino-S-triazine-2,4-diyl)[2,2,6,6-tetramethyl-4-piperidyl]imino]-hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino] [CAS No. 82451-48-7] commercially available from SUN CHEMICAL CO., LTD. under the tradename of Cyasorb UV-3346, 1,6-hexanediamine, N,N'-bis(1,2,2,6,6-pentamethyl-4-piperidyl)-, polymers with morpholine-2,4,6-trichloro-1,3,5-triazine [CAS No. 193098-40-7] commercially available under the tradename of Cyasorb UV-3529, 2,2,6,6-tetramethyl-4-piperidyl-C12-21 and C18 unsaturated fatty esters [CAS No. 167078-06-0] 10 commercially available under the tradename of Cyasorb UV-3853, and 3,5-di-t-butyl-4-hydroxybenzoic acid, n-hexadecyl ester [CAS No. 67845-93-6] commercially available under the tradename of Cyasorb UV-2908; dimethyl succinate-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine 15 polycondensate [CAS No. 65447-77-0] commercially available from Ciba Specialty Chemicals, K.K. under the tradename of Tinuvin 622 LD, poly[{6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl}{(2,2,6,6-tetramethyl-4-piperidyl)imino}-hexamethylene{(2,2,6,6-tetramethyl-4-piperidyl)imino}] [CAS 20 No. 71878-19-8] commercially available under the tradename of Chimassorb 944 LD, N,N'-bis(3-aminopropyl)ethylenediamine-2,4-bis[N-butyl-N-(1,2,2,6,6-pentamethyl-4-piperidyl)amino]-6-chloro-1,3,5-triazine condensate [CAS No. 106990-43-6] 25 commercially available under the tradename of Chimassorb 119 FL, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate [CAS No. 129757-67-1] commercially available under the tradename of Tinuvin 123, bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate [CAS No. 52829-07-9] commercially 30 available under the tradename of Tinuvin 770, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate [CAS No. 41556-26-7] 35 commercially available under the tradename of Tinuvin 765, and

bis(1,2,2,6,6-pentamethyl-4-piperidyl) 2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-n-butylmalonate [CAS No. 63843-89-0] commercially available under the tradename of Tinuin 144; hindered amines commercially available from Asahi Denka Kogyo Ltd. under the tradenames of ADEKA STAB LA-77, ADEKA STAB LA-57, ADEKA STAB LA-62, ADEKA STAB LA-67, ADEKA STAB LA-63, ADEKA STAB LA-68, ADEKA STAB LA-82 and ADEKA STAB LA-87; and hindered amines commercially available from Goodrich under the tradename of Goodrich UV-3034. If necessary, a combination of these basic materials may also be used.

Alkanol amines preferably have a boiling point of 50°C or above, more preferably 70°C or above. Specific examples thereof include N,N-diethylethanolamine, N,N-dimethylethanolamine, N-(2-aminoethyl)ethanolamine, N-methyldiethanolamine, N,N-dibutylethanolamine, N-methylethanolamine, triethanolamine, and trimethanolamine.

The photosensitive composition according to the present invention generally contains the above basic material in an amount of 0.01 to 10% by mass based on the mass of the modified polysilsesquiazane, depending upon the type and applications. When the content of the basic material is less than 0.01% by mass, the effect of preventing a change in dimension of pattern is unsatisfactory. On the other hand, when the content of the basic material exceeds 10% by mass, a large part of the acid produced from the photoacid generating agent upon light irradiation is trapped by the basic material, disadvantageously leading to a remarkable increase in level of sensitivity lowering. The amount of the basic material is preferably 0.02 to 5% by mass based on the mass of the modified polysilsesquiazane.

The photosensitive composition according to the present invention may further comprise a water-soluble compound as a shape stabilizer. The shape stabilizer refers to an agent which can increase the steepness of a side wall of the section of a pattern formed by removing the light exposed area.

As described above, in the modified polysilsesquiazane according to the present invention, the Si-N bond is cleaved by light irradiation, and the cleaved parts are then reacted with moisture in the atmosphere to give a silanol bond. In this case,

5 since the modified polysilsesquiazane is highly hydrophobic, the formation of the silanol bond rapidly takes place in a portion near the coating surface in contact with the moisture-containing atmosphere. In the coating in its inside not in contact with the moisture-containing atmosphere, however, as the portion is

10 closer to the interface of the substrate and the coating, the amount of water, which permeates and arrives at this portion through the coating surface, is smaller. Therefore, the formation of the silanol bond is less likely to occur. For this reason, the modified polysilsesquiazane coating has such a

15 sensitivity difference that the photosensitivity lowers from the surface toward the interface of the substrate. Therefore, as the portion is closer to the coating surface, the silanol bond is more easily formed and the portion is more easily dissolved and removed by the development. Consequently, the side wall of

20 the section of the pattern becomes gently sloped. This phenomenon is causative of a limitation on pattern refinement or improved resolution. In this case, when a water-soluble compound is added as the shape stabilizer, the side wall of the section of the pattern can be made steep and the resolution can

25 be enhanced. Specifically, the addition of the water-soluble compound can lower the hydrophobicity of the photosensitive coating and can accelerate access of water from the coating surface in contact with the moisture-containing atmosphere to the inside of the coating. Therefore, the difference in silanol

30 bond formation rate between the coating in its portion near the surface and the coating in its portion near the interface of the coating and the substrate, that is, sensitivity difference, becomes small. This can lower irradiation light energy necessary for satisfactorily dissolving and removing the coating

35 in its portion corresponding to the mask opening to a position near the interface of the coating and the substrate and, in its

turn, can lower energy of "light oozing" to the mask shielded part. In the part where the energy of "oozed light" has been reduced to a level that is too small to cleave the Si-N bond of the modified polysilsesquiazane, even when the part is exposed  
5 indirectly to the "oozed light," the silanol bond is not formed. Therefore, that part is not dissolved and removed during development. Consequently, in the mask shielded part, the dissolution and removal of that part is reduced, and the side wall of the section of the pattern is made steep, and most  
10 preferably vertical.

It could be easily understood that rendering the side wall of the section of the pattern steep can be achieved independently of the level of the photosensitivity of the photosensitive composition. Specifically, when the  
15 photosensitivity of the photosensitive composition in its part near the substrate is high, as described above, the side wall of the section of the pattern can be made steep by lowering the irradiation light energy. Further, for example, when the photosensitivity of the whole photosensitive composition has  
20 been lowered due to the addition of the water-soluble compound according to the present invention, in some cases, the irradiation light energy necessary for satisfactorily dissolving and removing the coating in its part corresponding to the opening of the mask to the position near the interface of the  
25 coating and the substrate should be enhanced. In this case, however, since the energy of the "oozed light" necessary for cleaving the Si-N bond in the modified polysilsesquiazane in its mask shielded part is also similarly enhanced, the side wall of the section of the pattern can be similarly made steep when the  
30 sensitivity difference of the coating is small. In short, the side wall of the section of the pattern can be made steep independently of the photosensitivity level of the photosensitive composition by reducing the difference in photosensitivity between the part near the coating in its surface and the coating  
35 in its part near the interface of the coating and the substrate.

Even when the water-soluble compound is insoluble in

neutral water, the water-soluble compound is useful so far as it is soluble in acidic or basic water. The reason for this is that, when the water-soluble compound is soluble in acidic water, the radiation exposed area is made acidic by an acid generated from the photoacid generating agent while, when the water-soluble compound is soluble in basic water, the penetration of the developer can be accelerated during development with an aqueous alkaline solution. In any case, access of water from the surface of the coating to the inside of the coating is accelerated, and, thus, the difference in sensitivity between the coating in its part near the surface and the coating in its part near the interface of the coating and the substrate becomes small.

The water-soluble compound according to the present invention may be a monomer or a polymer. A solubility of the water-soluble compound in neutral water, acidic water, or basic water of not less than about 0.01 g/100 mL suffices for contemplated results, and the water-soluble compound is not necessarily required to be easily soluble in the water. In this case, however, as described below, since the water-soluble compound is preferably homogeneously mixed with the photosensitive composition, the water-soluble compound should be satisfactorily miscible with the modified polysilsesquiazane and the solvents.

Specific examples of such compounds include 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2-nitro-4-aminotoluene, 3-nitro-2-aminotoluene, 3-nitro-4-aminotoluene, 4-nitro-2-aminotoluene, 5-nitro-2-aminotoluene, 6-nitro-2-aminotoluene, 4-nitrobenzene-azo-resorcinol, 1-(4-nitrobenzensulfonyl)-1H-1,2,4-triazole, 5-nitrobenzimidazole, 4-nitrobenzylacetate, 2-nitrobenzylalcohol, 3-nitrobenzylalcohol, 4-nitrobenzylalcohol, nitrocyclohexane, 1-nitropropane, 2-nitropropane, nifedipine, 2,7-dinitrofluorene, 2,7-dinitro-9-fluorenone, 3,3'-dinitrobenzophenone, 3,4'-dinitrobenzophenone, propylene carbonate, ethylene carbonate, amide compounds such as trifluoroacetamide, ammonium trifluoroacetate, water-

soluble acrylic polymers, water-soluble epoxy polymers, and water-soluble melamine polymers. Particularly suitable water-soluble compounds include 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2-nitro-4-aminotoluene, propylene carbonate, 5 ethylene carbonate, and water-soluble acrylic polymers.

The photosensitive composition according to the present invention may contain, as a shape stabilizer, the water-soluble compound in an amount of 0.01 to 50% by mass based on the mass of the modified polysilsesquiazane. The optimal mixing 10 ratio varies depending upon the properties of individual water-soluble compounds. However, when the content of the water-soluble compound is smaller than 0.01% by mass, the effect of improving the slope of the side wall of the pattern is small. On the other hand, when the content of the water-soluble 15 compound is larger than 50% by mass, problems associated with film properties after the development, such as defects and unsatisfactory strength occur. The content of the water-soluble compound in the mass of the modified polysilsesquiazane is preferably 0.05 to 40% by mass, more preferably 0.1 to 30% 20 by mass.

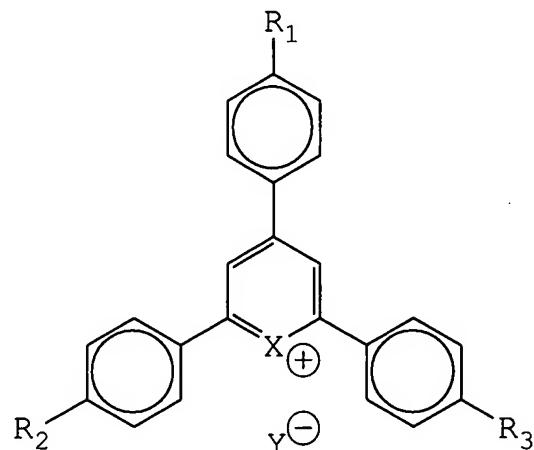
The photosensitive composition of the present invention may be prepared by adding the above photoacid generating agent and the basic material, optionally together with the water-soluble compound as the shape stabilizer, to the modified 25 polysilsesquiazane. The photoacid generating agent and the basic material are preferably homogeneously mixed with the modified polysilsesquiazane. Methods desirably usable for achieving the homogeneous mixing include one wherein the modified polysilsesquiazane is mixed with the photoacid 30 generating agent and the basic material while thorough stirring and one wherein each of them is diluted with a solvent which will be described later followed by mixing. In particular, in the mixing, when the photoacid generating agent and the basic material are solid, preferably, they are dissolved in a solvent 35 before mixing. At the time of the addition of the photoacid generating agent and the water-soluble compound, the

temperature and the pressure are not particularly limited, and the addition may be carried out at room temperature under the atmospheric pressure. In order to avoid the excitation of the photoacid generating agent, the procedure from the addition of  
5 the photoacid generating agent to the step of development which will be described later is preferably carried out in an environment free from wavelengths photosensitive to the photoacid generating agent used, preferably in a dark place.

In some cases, mixing a sensitizing dye into the  
10 photosensitive composition according to the present invention is advantageous. For some photoacid generating agents, for example, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone, the excitation wavelength region of the photoacid generating agent per se is shorter than about 330 nm. When light  
15 irradiation is carried out using an excimer laser, such as a KrF (248 nm) or ArF (193 nm) excimer laser, the photoacid generating agent is directly excited. Therefore, in this case, the use of the sensitizing dye is not necessary. When an inexpensive light source such as a high pressure mercury lamp  
20 (360 to 430 nm) is used, however, the combined use of the photosensitive composition and a sensitizing dye excited by this wavelength region can realize indirect excitation of the photoacid generating agent. Thus, the combined use of the photosensitive composition and the sensitizing dye can realize  
25 patterning of the photosensitive composition according to the present invention with a conventional inexpensive light source.

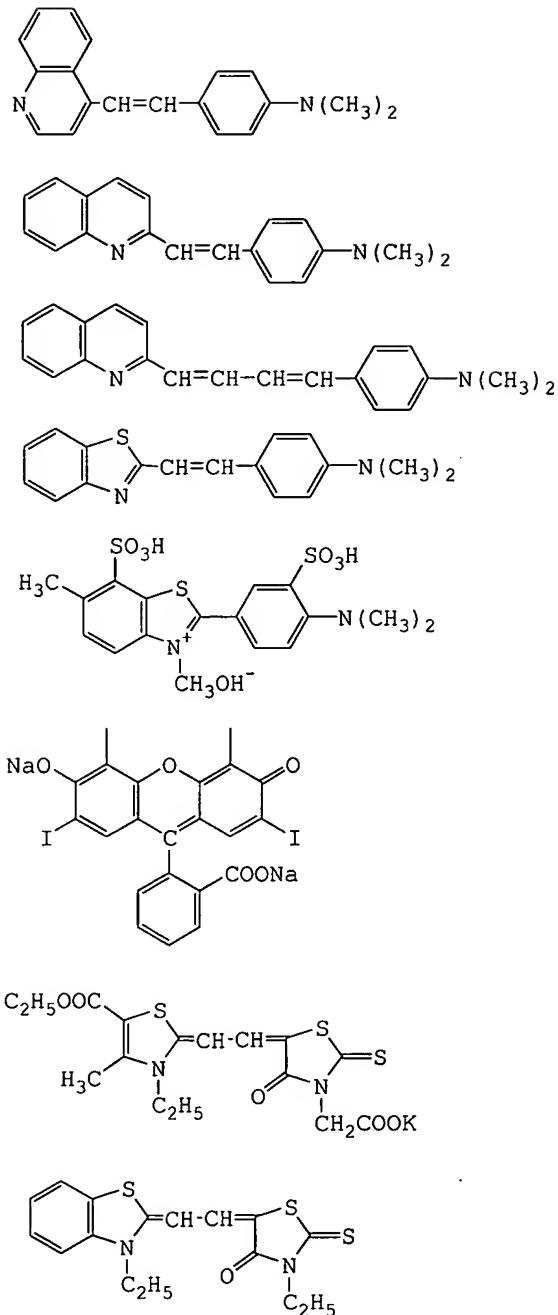
Sensitizing dyes usable in the photosensitive composition according to the present invention include coumarin, ketocoumarin, their derivatives, thiopyrilium salts and the like,  
30 specifically p-bis(o-methylstyryl)benzene, 7-dimethylamino-4-methylquinolone-2,7-amino-4-methylcoumarin, 4,6-dimethyl-7-ethylaminocoumarin, 2-(p-dimethylaminostyryl)-pyridylmethyliodide, 7-diethylaminocoumarin, 7-diethylamino-4-methylcoumarin, 2,3,5,6-1H,4H-tetrahydro-8-methylquinolizino-  
35 <9,9a,1-gh>coumarin, 7-diethylamino-4-trifluoromethylcoumarin, 7-dimethylamino-4-

trifluoromethylcoumarin, 7-amino-4-trifluoromethylcoumarin, 2,3,5,6-1H,4H-tetrahydroquinolizino-<9,9a,1-gh>coumarin, 7-ethylamino-6-methyl-4-trifluoromethylcoumarin, 7-ethylamino-4-trifluoromethylcoumarin, 2,3,5,6-1H,4H-tetrahydro-9-carboethoxyquinolizino-<9,9a,1-gh>coumarin, 3-(2'-N-methylbenzimidazolyl)-7-N,N-diethylaminocoumarin, N-methyl-4-trifluoromethylpiperidino-<3,2-g>coumarin, 2-(p-dimethylaminostyryl)-benzothiazolylethyliodide, 3-(2'-benzimidazolyl)-7-N,N-diethylaminocoumarin, 3-(2'-benzothiazolyl)-7-N,N-diethylaminocoumarin, and pyrilium salts 10 and thiopyrilium salts represented by the following formula.



X	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Y
S	OC <sub>4</sub> H <sub>9</sub>	H	H	BF <sub>4</sub>
S	OC <sub>4</sub> H <sub>9</sub>	H	H	BF <sub>4</sub>
S	OC <sub>4</sub> H <sub>9</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	BF <sub>4</sub>
S	H	OCH <sub>3</sub>	OCH <sub>3</sub>	BF <sub>4</sub>
S	N(CH <sub>3</sub> ) <sub>2</sub>	H	H	ClO <sub>2</sub>
O	OC <sub>4</sub> H <sub>9</sub>	H	H	SbF <sub>6</sub>

15 Specific examples of other sensitizing dyes include the following compounds.



Particularly suitable sensitizing dyes include 7-diethylamino-4-methylcoumarin and 7-diethylamino-4-trifluoromethylcoumarin.

When the sensitizing dye is additionally used, the content of the sensitizing dye in the photosensitive composition according to the present invention may be generally 0.05 to 50% by mass, preferably 1 to 20% by mass, based on the mass

of the modified polysilsesquiazane.

When the sensitizing dye is mixed into the photosensitive composition according to the present invention, the resultant film is sometimes colored. When the photosensitive composition of the present invention is used to form a patterned interlayer insulation film which is then applied to display devices or the like, however, in some cases, the interlayer insulation film after baking should be transparent to visible light. Even in this case, the photoacid generating agent contained in the photosensitive composition according to the present invention can decompose the sensitizing dye during baking of the film to render the interlayer insulation film after baking transparent to light.

Further, an interlayer insulation film having a higher level of transparency can be formed by separately adding an oxidation catalyst, which is not directly involved in the photoreaction but can decompose the sensitizing dye during baking of the film, to the photosensitive composition of the present invention. Examples of such oxidation catalysts include organic compounds and fine particles of metals such as palladium propionate, palladium acetate, platinum acetylacetone, platinum ethylacetone, fine particles of palladium, and fine particles of platinum. When the oxidation catalyst is added, the content of the oxidation catalyst in the photosensitive composition according to the present invention may be generally 0.05 to 10% by mass, preferably 0.1 to 5% by mass, based on the mass of the modified polysilsesquiazane. Further, the addition of the oxidation catalyst can realize decomposition of the unnecessary dye for decoloration, as well as the acceleration of the conversion of the modified polysilsesquiazane to a ceramic.

When a solvent is used, preferred are: aromatic compounds such as benzene, toluene, xylene, ethylbenzene, diethylbenzene, trimethylbenzene, and triethylbenzene; cyclohexane; cyclohexene; decahydronaphthalene; dipentene; saturated hydrocarbon compounds such as n-pentane, i-

pentane, n-hexane, i-hexane, n-heptane, i- heptane, n-octane, i-octane, n-nonane, i-nonane, n-decane, and i-decane; ethylcyclohexane; methylcyclohexane; p-menthane; ethers such as dipropylether and dibutylether; ketones such as methyl isobutyl ketone (MIBK); and esters such as butyl acetate, cyclohexyl acetate, and butyl stearate. When these solvents are used, two or more of them may be used as a mixture from the viewpoint of regulating the solubility of the modified polysilsesquiazane and the evaporation rate of the solvent.

The amount (content) of the solvent is selected to provide good workability depending upon a coating method adopted. Further, since the amount (content) of the solvent varies depending upon the average molecular weight, the molecular weight distribution, and the structure of the modified polysilsesquiazane used, the solvent may be properly mixed freely. When the stability of the modified polysilsesquiazane and the productivity are taken into consideration, however, the concentration of the modified polysilsesquiazane is preferably 0.1 to 50% by mass, more preferably 0.1 to 40% by mass.

Further, the photosensitive composition according to the present invention may optionally contain a suitable filler and/or an extender. Examples of fillers include fine powder of inorganic oxides including silica, alumina, zirconia, and mica and inorganic nonoxides such as silicon carbide and silicon nitride. The addition of powder of a metal such as aluminum, zinc, or copper is also possible for some application. These fillers may be in various forms such as acicular (including whisker), particulate, and flaky forms which may be used either solely or as a mixture of two or more. The size of particles of these fillers is preferably smaller than the thickness of a film formed by single application. The amount of the filler added is in the range of 0.05 to 10 parts by mass, particularly preferably in the range of 0.2 to 3 parts by mass, based on one part by mass of the modified polysilsesquiazane.

The photosensitive composition according to the present invention may optionally contain various pigments, leveling

agents, antifoaming agents, antistatic agents, ultraviolet absorbers, pH adjustors, dispersants, surface modifiers, plasticizers, drying accelerators, and flow preventives.

The present invention also provides a method for forming  
5 a patterned interlayer insulation film using the above  
photosensitive composition. Specifically, the method according  
to the present invention comprises the steps of: forming a  
coating of the above photosensitive composition for an  
interlayer insulation film; applying light pattern-wise to the  
10 coating; and dissolving and removing the coating in its exposed  
area.

The coating of the photosensitive composition according  
to the present invention may be formed on a suitable substrate  
such as a silicon substrate or a glass substrate by a  
15 conventional coating method such as dipping, roll coating, bar  
coating, brush coating, spray coating, flow coating, or spin  
coating. When the substrate is a film, the coating may be  
formed by gravure coating. If desired, the step of drying the  
coating may be provided separately.

20 The photosensitive composition may be coated once or  
twice or more repeatedly according to need to give a desired  
coating thickness. According to the present invention, the  
selection of the linking group other than the silazane bond can  
improve the film thickness limit. Therefore, a crack-free  
25 interlayer insulation film having a thickness of not less than 5.0  
 $\mu\text{m}$ , preferably not less than 10.0  $\mu\text{m}$ , can be provided.

After the formation of the coating of the photosensitive  
composition according to the present invention, the coating is  
preferably prebaked (heat-treated) from the viewpoints of  
30 drying the coating and reducing the amount of degassing in a  
later step. The step of prebaking may be generally carried out  
at 40 to 200°C, preferably 60 to 120°C, for 10 to 180 sec,  
preferably 30 to 90 sec, in the case of prebaking using a hot  
plate and for 1 to 30 min, preferably 5 to 15 min, in the case of  
35 prebaking in a clean oven.

The formation of the coating of the photosensitive

composition according to the present invention and optional prebaking are followed by the application of light to the coating in a pattern-wise manner. Light sources usable herein include high pressure mercury lamps, low pressure mercury lamps, 5 metal halide lamps, and excimer lasers. Light with wavelengths of 360 to 430 nm (from a high pressure mercury lamp) is generally used as irradiation light except for ultrafine patterning in the case of semiconductors or the like. Among others, in the case of liquid crystal display devices, light with a wavelength of 430 nm is in many cases used. In this case, as 10 described above, the combination of the photosensitive composition according to the present invention with the sensitizing dye is advantageous.

The energy of the irradiation light may vary depending 15 upon the light source and the desired film thickness. In general, however, the energy is 5 to 4,000 mJ/cm<sup>2</sup>, preferably 10 to 2,000 mJ/cm<sup>2</sup>. When the energy is less than 5 mJ/cm<sup>2</sup>, the modified polysilsesquiazane is not satisfactorily decomposed. On the other hand, when the energy is higher than 4,000 20 mJ/cm<sup>2</sup>, the exposure is excessive, sometimes leading to halation.

A conventional photomask may be used for pattern-wise irradiation, and the photomask is well known to a person having ordinary skill in the art.

25 The irradiation may be generally carried out in an environment such as an ambient atmosphere (the air) or a nitrogen atmosphere. Alternatively, an atmosphere enriched with oxygen may be adopted from the viewpoint of accelerating the decomposition of the modified polysilsesquiazane.

30 Upon exposure of a coating of the photosensitive composition to light in a pattern-wise manner, Si-N bonds of the modified polysilsesquiazane in the exposed area of the coating are cleaved, and the cleaved parts are reacted with moisture in an atmosphere to give silanol (Si-OH) bonds and, thus, to 35 decompose the modified polysilsesquiazane. When the coating after the exposure is developed, the photosensitive composition

in its exposed area is removed while the unexposed area stays on the substrate to form a pattern (a positive-working pattern). Since the residual modified polysilsesquiazane is not substantially swollen in a developer which will be described later,  
5 the pattern of the irradiated light is substantially completely consistent with the pattern of the decomposed and removed modified polysilsesquiazane. Therefore, good pattern accuracy (resolution) can be provided.

In the removal of the exposed area of the modified  
10 polysilsesquiazane composition, that is, in the development, an aqueous alkaline solution may be used as a developer. Aqueous alkaline solutions usable herein include aqueous solutions of tetramethyl ammonium hydroxide (TMAH), sodium silicate, sodium hydroxide, potassium hydroxide and the like.  
15 In the development according to the present invention, the use of an about 2% aqueous TMAH solution, which is a standard alkaline developer in the industry, is convenient.

The time necessary for the development is generally 0.1 to 5 min, preferably 0.5 to 3 min, although it varies depending  
20 upon the film thickness and the solvent used. The development treatment temperature is generally 20 to 50°C, preferably 20 to 30°C.

Compounds known as the so-called "dissolution preventive" in the art may be added to the photosensitive  
25 composition according to the present invention from the viewpoint of enhancing the development efficiency. A conventional dissolution preventive prevents the elution of the polymer in the unexposed area of the coating into an alkaline developer by taking advantage of the hydrophobicity. In the  
30 exposed area, however, upon exposure or upon the action of the photoacid generating agent, the dissolution preventive per se is decomposed to develop hydrophilicity, thereby accelerating the decomposition of the polymer. As described above, the modified polysilsesquiazane according to the present invention  
35 is not dissolved in the developer and thus does not substantially enjoy the merit of dissolution preventive function of the

dissolution preventive in the unexposed area. However, it has been found that, in the exposed area, the dissolution acceleration function can be advantageously exhibited. Specifically, the addition of the so-called "dissolution preventive" to the photosensitive composition according to the present invention can improve the development efficiency by virtue of increased dissolution rate of the exposed area. Specific examples of dissolution preventives include t-butoxycarbonylated (hereinafter referred to as "t-BOC") catechol, t-BOC hydroquinone, t-butyl benzophenone-4,4'-dicarboxylate, and t-butyl 4,4'-oxydibenzene. The amount of the dissolution preventive added may be in the range of 0.1 to 40% by mass, preferably in the range of 1 to 30% by mass, based on the photosensitive composition.

Upon the development, the photosensitive modified polysilsesquiazane composition in its exposed area is removed to complete patterning. In order to use the patterned modified polysilsesquiazane film as an interlayer insulation film, the patterned modified polysilsesquiazane film may be allowed to stand for a long period of time or may be baked to convert the patterned modified polysilsesquiazane film to an excellent silica-based ceramic film having high heat resistance, low permittivity, transparency and other properties. When the modified polysilsesquiazane film is allowed to stand after the development, standing generally in an ambient atmosphere (in the air at room temperature) for a long period of time, for example, for one day or longer suffices for contemplated results. On the other hand, when the modified polysilsesquiazane film is baked, the baking temperature is generally 50 to 1000°C, preferably 100 to 1000°C, more preferably 150 to 450°C, although it may vary depending upon the type of the modified polysilsesquiazane used and the heat resistance of substrates, electronic components and the like. The baking time is generally not less than 5 min, preferably not less than 10 min. The baking may be generally carried out in an ambient atmosphere (in the air). An atmosphere having increased

oxygen content and/or partial pressure of water vapor, however, may be adopted from the viewpoint of accelerating the oxidation of the modified polysilsesquiazane.

The interlayer insulation film provided by the present invention has a permittivity of not more than 5 and, in some cases, a permittivity of not more than 3.3, and a resistivity of not less than  $10^{13}$   $\Omega\text{cm}$ .

### EXAMPLES

10 The following examples further illustrate the present invention.

#### Example 1

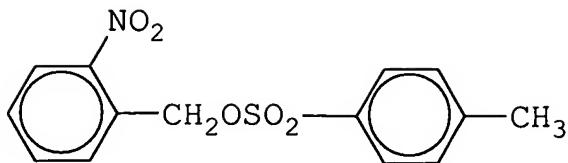
15 The inside of a four-necked flask equipped with a gas inlet tube, a mechanical stirrer, and a Dewar condenser was purged with dry nitrogen. Thereafter, a starting solution was prepared in the flask by diluting methyltrichlorosilane ( $\text{CH}_3\text{SiCl}_3$ ) and 10% by mole, based on the amount of methyltrichlorosilane, of 1,4-bis(dimethylchlorosilyl)benzene ( $\text{ClSi}(\text{CH}_3)_2\text{PhSi}(\text{CH}_3)_2\text{Cl}$ ) with pyridine to give a total monomer concentration of 20% by mass. Ammonia ( $\text{NH}_3$ ) was mixed little by little into the starting solution through the gas inlet tube to cause an ammonolysis reaction.

20 After the completion of the reaction, a copolymer represented by  $-(\text{SiCH}_3(\text{NH})_{1.5})_n-$  and  $-(\text{SiMe}_2\text{PhSiMe}_2(\text{NH}))_n-$  was obtained. This polymer had a number average molecular weight of 2406 and had a weight average molecular weight (as determined using polystyrene as a standard) of 35225.

25 Next, the copolymer was subjected to solvent displacement to give a propylene glycol monomethyl ether acetate (PGMEA) solution having a polymer solid content of 20% by mass.

30 To the solution was added 0.5% by mass, based on the mass of the polymer, of the following photoacid generating agent PAG-1.

35 PAG-1



Next, the solution was divided into four parts, and didodecylamine in an amount of 0%, 0.5%, 1%, and 2% based on the mass of the polymer was added as the basic material to  
5 the respective divided solutions.

The solutions thus obtained were spin coated on a silicon wafer at a speed of rotation of 1000 rpm, and the coating was prebaked at 100°C for one min. As a result, a 1.2  $\mu\text{m}$ -thick thin film was formed.

10 This thin film was introduced into an electron beam exposure system (model: ELS 6600B, manufactured by Erionics Co.) and was exposed to a space pattern of 0.2  $\mu\text{m}$  at an intensity of 10  $\mu\text{C}/\text{cm}^2$ . Next, this thin film was taken out of the system, was allowed to stand in a clean room (23°C) for 3  
15 hr, was then exposed to a humidified atmosphere of 25°C and 80%RH for 5 min, and was then immersed in a 2.38% aqueous tetramethylammonium hydroxide (TMAH) solution (23°C) for one min. As a result, the areas exposed to the electron beam were dissolved, and the space pattern was transferred. The  
20 space pattern width obtained for the above four solutions are shown in Table 1.

Table 1

Amount of didodecylamine added, %	Formed space pattern width, $\mu\text{m}$
0	0.4
0.5	0.3
1	0.25
2	0.2

25 Table 1 shows that the addition of a basic material reduces a change in dimension of the pattern. Further, it is apparent that the level of a change in dimension of the pattern decreases with increasing the amount of the basic material

added, and, when the amount of the basic material added is 2%, the irradiation pattern is faithfully transferred.

**Example 2**

The inside of a four-necked flask equipped with a gas inlet tube, a mechanical stirrer, and a Dewar condenser was purged with dry nitrogen. Thereafter, a starting solution was prepared in the flask by diluting methyltrichlorosilane ( $\text{CH}_3\text{SiCl}_3$ ) and 5% by mole, based on the amount of methyltrichlorosilane, of 1,5-dichlorohexamethyltrisiloxane ( $(\text{ClSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{Cl})$ ) and 5% by mole, based on the amount of methyltrichlorosilane, of diphenyldichlorosilane ( $\text{Ph}_2\text{SiCl}_2$ ) with pyridine to give a total monomer concentration of 20% by mass. Ammonia ( $\text{NH}_3$ ) was mixed little by little into the starting solution through the gas inlet tube to cause an ammonolysis reaction.

After the completion of the reaction, a copolymer represented by  $-(\text{SiCH}_3(\text{NH})_{1.5})-$ ,  $-(\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2)-$  and  $-(\text{SiPh}_2(\text{NH}))-$  was obtained. This polymer had a number average molecular weight of 1056 and had a weight average molecular weight (as determined using polystyrene as a standard) of 4566.

Next, the copolymer was subjected to solvent displacement to give a PGMEA solution having a polymer solid content of 30% by mass.

To the solution were added 5% by mass, based on the mass of the polymer, of 3,3',4,4'-tetra(*t*-butylperoxycarbonyl)benzophenone as the photoacid generating agent and 3% by mass, based on the mass of the polymer, of 7-amino-4-methyl coumarin as the sensitizing dye.

Next, to the solution was added 1% by mass, based on the mass of the polymer, of hindered amine or alkanolamine as the basic material. Poly[(6-morpholino-S-triazin-2,4-diyl)[2,2,6,6-tetramethyl-4-piperidyl]imino]-hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino] (basic material A) and bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (basic material B) were used as the hindered amine, and

triethanolamine (basic material C) and N,N-dimethylethanolamine (basic material D) were used as the alkanolamine.

The solutions thus obtained were spin coated on a silicon wafer at a speed of rotation of 2000 rpm, and the coating was prebaked at 90°C for one min. As a result, a 0.9 μm-thick thin film was formed.

This thin film was introduced into a contact aligner (PLA-501 manufactured by Canon Inc.) and was exposed to a space pattern of 1 μm. Next, this thin film was taken out of the aligner, was allowed to stand in a clean room (23°C) for 5 hr, was then exposed to a humidified atmosphere of 25°C and 80%RH for 2 min, and was then immersed in a 2.38% aqueous TMAH solution (23°C) for one min. As a result, the exposed areas were dissolved, and the space pattern was transferred. The space pattern width measured under an electron microscope is shown in Table 2 below. The results shown in Table 2 show that the addition of various basic materials reduces a change in dimension of pattern.

20

Table 2

Basic material	Width dimension after standing, μm	Dimensional change , μm
None	7	6
A	1.2	0.2
B	2	1
C	2.5	1.5
D	1.5	0.5

#### Industrial Applicability

As described above, the addition of a basic material to a polysilsesquiazane photosensitive composition containing a photoacid generating agent can prevent a change in dimension of pattern caused by diffusion of an acid produced in exposed areas.